

# Partial Pressures in Liquid Mixtures and Osmotic Pressures

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When an osmotic system is composed of 1- and 0-species particles, which are confined to the volumes,  $V \equiv V_a + V_b$  and  $V_b$ , by the wall pressures,  $P_1^{w_a}$  and  $P_0^{w_b}$ , respectively, we obtain a law of partial pressures as described in the forms:  $P_1^{w_a} = P_{1b} + \Gamma$ ,  $P_0^{w_b} = P_{0b} - \Gamma$  and  $P = P_0^{w_b} + P_1^{w_a} = P_{0b} + P_{1b}$  for the total pressure  $P$ . Here, the partial pressures,  $P_{\alpha b}$ , are given by the virial equation in the solution of 0- and 1-species in  $V_b$ , and the pressure difference  $\Gamma$  on a semipermeable membrane appears owing to the presence of density discontinuity at the membrane. On the basis of this result, we show that the partial pressures defined by the wall pressures are measurable in liquid mixtures, and satisfy the law of partial pressures, which gives the total pressure by the sum of partial pressures. Also, the partial pressures are shown to play an important role in treating the vapor-liquid equilibrium as well as osmotic systems. In fluid physiology, the partial pressure of water in solutions is important to determine water balance in body fluids.

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## I. INTRODUCTION

At the present stage, it is a common belief that the law of partial pressures is only applicable to ideal gases as Dalton's law, although there is no proof for this applicable limitation. Contrary to the above belief, we have proven that the total pressure of the electron-nucleus mixture such as liquid metals and plasmas can be represented as the sum of the electron and nuclear pressures, which are defined by the wall potentials confining the electrons and nuclei in the finite volume, respectively [1, 2]. This result makes a contradiction to the common belief mentioned above, since the concept of 'partial pressure' is introduced in treating interacting systems. To clarify this contradiction, we investigate here the problem of partial pressures for liquid and real gas mixtures.

Let us consider an osmotic system: a sugar-solution compartment separated from a pure-water compartment by a semipermeable membrane, for example. The osmotic pressure, that is, the pressure on the membrane exerted by the sugar is different from the internal sugar pressure in the solution [3]. This fact may give rise to a confusion that the law of partial pressures can not be applied to a sugar-water mixture confined in a finite volume by the wall. In this investigation, in the first place, we show that, in general, for a mixture confined by the wall to a finite volume, the partial pressure of each component can be defined by the pressure on the wall exerted by each component, and the total pressure is represented by the sum of these partial pressures. In the second place, on

the basis of first principles (the virial theorem) we prove in the general situation an experimental fact found in the molecular dynamic simulation performed by Itano *et. al.* [3]; that is, the fact that the "partial" pressure of the solute (such as sugar) is higher than the semi-membrane pressure confining the solute by a difference  $\Gamma$ , and the solvent (water) pressure in the solution is lower than the wall pressure confining the solvent by the same difference  $\Gamma$  in the osmotic system. In the third place, the partial pressures are shown to be measurable and important physical quantities by using the results found in osmotic systems; as a consequence, the law of partial pressures for interacting systems is proven as a significant physical law.

With this respect, when we take the sugar solution and the pure water separated by the membrane as a whole one system confined to a finite volume, there is a step-function-like jump of the sugar-density on the membrane, since the sugar exists only in the solution. From this, we find that partial pressures of sugar and water are related to the osmotic and wall pressures by use of the pressure difference caused by the density discontinuity on the membrane. In addition, the vapor-liquid equilibrium is shown to be a special state of an osmotic system, which is described by partial pressures.

## II. PARTIAL PRESSURES AND OSMOTIC PRESSURES

At the beginning, we write up the basic equations and the concept "wall pressure", necessary to derive the pressure relations in this section.

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### (I) Virial theorem for one particle:

In the system confined by the wall potential  $U^w$  to the volume  $V$  at a temperature  $T$ , where the particles are interacting via a binary potential  $v_{ij}$  under the external potential  $U^{\text{ex}}$ , the virial theorem for one arbitrary  $i$ -particle [1] is written as

$$2\langle p_i^2/2m_i \rangle = \langle \mathbf{r}_i \cdot \nabla_i (U + U^w) \rangle = 3k_B T. \quad (1)$$

Here,  $\mathbf{p}_i$  and  $\mathbf{r}_i$  are the momentum and position of  $i$ -particle, respectively, and  $U \equiv \sum_{i<j} v_{ij} + U^{\text{ex}}$ . In the above, the bracket  $\langle \rangle$  denotes the ensemble average.

### (II) Wall pressure:

When a fluid is confined by the wall pressure  $P^w$  to a finite volume  $V$ , the wall pressure  $P^w$  is in balance with the hydrostatic pressure  $P$ :  $P^w = P$  just at the surface, thermodynamically; an external force  $F$  on the wall with a surface  $S$  provides the wall pressure  $P^w = F/S$ . Note that this relation is derived from a fundamental assumption based on the virial theorem (1) as shown below. The wall pressure  $P^w$  caused by the wall potential  $U^w$  on the particles is defined by

$$-\oint_{\partial V} P^w \mathbf{r} \cdot d\mathbf{S} \equiv -\sum_{i \in V} \langle \mathbf{r}_i \cdot \nabla_i U^w \rangle = \sum_{i \in V} \langle \mathbf{r}_i \cdot \mathbf{F}_i^w \rangle. \quad (2)$$

The virial theorem (1) provides the basis for the standard assumption concerning the relation between the force exerted by the wall on the particles and the hydrostatic pressure  $P$ :

$$\oint_{\partial V} P^w \mathbf{r} \cdot d\mathbf{S} \equiv \sum_i \langle \mathbf{r}_i \cdot \nabla_i U^w \rangle = \oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S}, \quad (3)$$

that is,

$$P^w = P = \sum_{i \in V} \left[ 2\langle \frac{p_i^2}{2m} \rangle - \langle \mathbf{r}_i \cdot \nabla_i U \rangle \right] / 3V, \quad (4)$$

when the external potential  $U^{\text{ex}}$  becomes zero inside the boundary surface  $\partial V$  to provide a constant pressure on  $\partial V$ . Hereafter, we denote the surface of a volume  $V$  by the symbol  $\partial V$ . Usually, the wall pressure  $P^w$  is *omitted* in the virial equation in the above, but it is important to treat osmotic systems. When the wall with a surface  $L^2$  is movable such as a membrane or a piston, an external force  $F$  on the wall provides the wall pressure  $P^w = F/L^2$  to keep the wall at rest. Therefore, it should be kept in mind that the wall pressure  $P^w$  represents also the experimentally *measurable* external pressure, as well as the pressure exerted by the fluid on the wall in addition to the wall pressure acting on the fluid. Thermodynamically, the wall potential  $U^w$  is assumed to be perfectly elastic and becomes abruptly infinite at the surface  $\partial V$ , and hence the density of the system becomes uniform from just inside the wall.

### (III) The virial equation for an arbitrary volume $\Omega$ in the system:

The virial equation is expressed by (4), and written for an arbitrary volume  $\Omega$  in  $V$  in the forms [4–7]:

$$\oint_{\partial \Omega} P \mathbf{r} \cdot d\mathbf{S} = \int_{\Omega} (3P + \mathbf{r} \cdot \nabla P) d\mathbf{r} \quad (5a)$$

$$= \sum_{i \in \Omega} \left[ 2\langle \frac{p_i^2}{2m} \rangle - \langle \mathbf{r}_i \cdot \nabla_i U \rangle \right]. \quad (5b)$$

### (IV) Discontinuous pressure:

In the case where the pressure  $P$  has a uniform but different pressure in each of the two domains,  $V_a$  and  $V_b$  ( $V = V_a + V_b$ ), separated by a surface  $S (= \partial V_b)$  of the volume  $V_b$  involved in the volume  $V$ , we obtain the following relation:

$$\begin{aligned} \oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S} &= \oint_{\partial V_a} P \mathbf{r} \cdot d\mathbf{S} + \oint_{\partial V_b} P \mathbf{r} \cdot d\mathbf{S} \\ &+ [P(S^{\text{out}}) - P(S^{\text{in}})] \oint_{\partial V_b} \mathbf{r} \cdot d\mathbf{S}. \end{aligned} \quad (6)$$

Here,  $P(S^{\text{out}}) \equiv \lim_{\epsilon \rightarrow 0} P(S_{+\epsilon})$  and  $P(S^{\text{in}}) \equiv \lim_{\epsilon \rightarrow 0} P(S_{-\epsilon})$ . Symbols,  $S_{+\epsilon}$  and  $S_{-\epsilon}$ , denote a surface  $S$  shifted outside by  $\epsilon$  and that shifted inside, respectively. In this case the surface integral  $\oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S}$  cannot be calculated by the volume integral  $\int_V \nabla[P \mathbf{r}] dV$  due to the discontinuity of pressure in the volume. Instead of using the volume integral, we can evaluate the surface integral by using the identical relation:  $\oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S} = [\oint_{\partial V} P \mathbf{r} d\mathbf{S} - \oint_{S_{+\epsilon}} P \mathbf{r} d\mathbf{S}] + [\oint_{S_{+\epsilon}} P \mathbf{r} d\mathbf{S} - \oint_{S_{-\epsilon}} P \mathbf{r} d\mathbf{S}] + \oint_{S_{-\epsilon}} P \mathbf{r} d\mathbf{S}$ , which leads to (6) in the limit  $\epsilon \rightarrow 0$ , with help of  $\lim_{\epsilon \rightarrow 0} [\oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S} - \oint_{S_{+\epsilon}} P \mathbf{r} \cdot d\mathbf{S}] = \oint_{\partial V_a} P \mathbf{r} \cdot d\mathbf{S}$ .

When a mixture composed of two types of species, 0 and 1, is confined by wall potentials,  $U_0^w$  and  $U_1^w$ , for each component to the same volume  $V$  with the total pressure  $P$ , the partial pressure  $P_\alpha$  can be defined by the pressure  $P_\alpha^w$  on the wall exerted by particles of  $\alpha$ -species as follows:

$$\begin{aligned} \oint_{\partial V} P_\alpha \mathbf{r} \cdot d\mathbf{S} &= \oint_{\partial V} P_\alpha^w \mathbf{r} \cdot d\mathbf{S} \equiv \sum_{i \in \alpha} \langle \mathbf{r}_i \cdot \nabla_i U_\alpha^w \rangle \\ &= \sum_{i \in \alpha} \left[ 2\langle \frac{p_i^2}{2m_\alpha} \rangle - \langle \mathbf{r}_i \cdot \nabla_i U \rangle \right], \end{aligned} \quad (7a)$$

which is obtained from the virial theorem for one particle (1). Thus, when the interatomic interaction is via binary potentials  $v_{\alpha\beta}(r)$ , the partial pressure  $P_\alpha$  can be written in the form of the virial equation [8]:

$$\begin{aligned} P_\alpha^w = P_\alpha &= k_B T \rho_\alpha - \frac{1}{6} \rho_\alpha^2 \int r \frac{dv_{\alpha\alpha}(r)}{dr} g_{\alpha\alpha}(r) d\mathbf{r} \\ &+ \sum_{i \in \alpha} \langle \mathbf{r}_i \cdot \mathbf{F}_i^\alpha \rangle / 3V, \end{aligned} \quad (7b)$$

in terms of the radial distribution functions  $g_{\alpha\beta}(r)$  and the density  $\rho_\alpha$  of  $\alpha$ -component. Here,  $\mathbf{F}_i^\alpha$  indicates the total force on  $i$ -particle of  $\alpha$ -species exerted by all particles of different species ( $\bar{\alpha}$ ) to  $\alpha$ , defined by  $\mathbf{F}_i^\alpha \equiv$

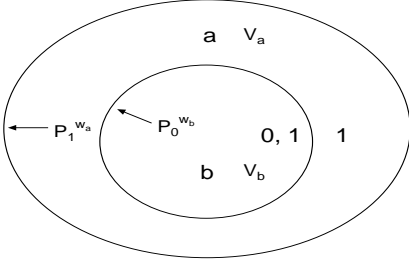


FIG. 1. An osmotic system composed of 1- and 0-species particles, which are confined to the volumes,  $V \equiv V_a + V_b$  and  $V_b$ , by the wall pressures,  $P_1^{w_a}$  and  $P_0^{w_b}$ , respectively.

$-\sum_{l \in \bar{\alpha}} \nabla_i v_{01}(|\mathbf{r}_i - \mathbf{r}_l|)$ , and these forces satisfy the following relation:

$$\sum_{i \in 0} \langle \mathbf{r}_i \cdot \mathbf{F}_i^0 \rangle + \sum_{l \in 1} \langle \mathbf{r}_l \cdot \mathbf{F}_l^1 \rangle = -V \rho_0 \rho_1 \int r \frac{dv_{01}(r)}{dr} g_{01}(r) d\mathbf{r}. \quad (8)$$

Also, the total pressure  $P$  is the sum of partial pressures  $P_\alpha$  defined by (7):  $P = P_0 + P_1$ , since the total pressure  $P$  is defined by the virial theorem:  $\oint_{\partial V} P \mathbf{r} \cdot d\mathbf{S} = \oint_{\partial V} P^w \mathbf{r} \cdot d\mathbf{S} \equiv \sum_\alpha \sum_{i \in \alpha} \langle \mathbf{r}_i \cdot \nabla_i U_\alpha^w \rangle$ , for a mixture confined by the wall pressure  $P^w$ . This is referred to as the law of partial pressures.

Next, we examine the relation between the osmotic pressure and the partial pressure in a solution. Let us consider a system where the 1-species particles and the 0-species particles are confined to the volume  $V$  and the volume  $V_b$  (contained in  $V$ ) by the wall pressures,  $P_1^{w_a}$  on  $\partial V$  and  $P_0^{w_b}$  on  $\partial V_b$ , respectively, as shown in Fig. 1 with  $V_a \equiv V - V_b$ . Here, the wall  $w_b$  becomes equivalent to a semipermeable membrane. In thermodynamics, the volumes,  $V$  and  $V_b$ , are defined by using the wall potentials which are perfectly elastic and become abruptly infinite at surfaces. Therefore in this system, the density and pressure of 0-species particles become zero in  $V_a$  and jumps to  $\rho_{0b}$  and  $P_{0b}$  in  $V_b$ , respectively, with the boundary  $S_b (\equiv \partial V_b)$  forming a discontinuity surface in  $V$ . Because of this discontinuity surface  $S_b$ , the formula to calculate pressures (5a) with use of the volume integral leads to infinite divergence due to the term  $\nabla P(\mathbf{r})$  involved in the integrand of (5a). The virial theorem, (5) and (1), avoiding this divergence with the help of (6) generates the relations between discontinuous quantities. In treating the osmotic system, it should be kept in mind that Eq. (1) ensures to define the partial pressure of  $\alpha$ -component in a mixture by the sum only of  $i$  belonging to  $\alpha$ -component ( $i \in \alpha$ ). As this result, we can obtain the relations concerning  $P_1^{w_a}$  and  $P_0^{w_b}$  for each component with the help of (6) and the virial theorem below.

For the case of 1-species, the partial pressure  $P_1(\mathbf{r})$  has different uniform pressures,  $P_{1b}$  and  $P_{1a}$ , in the inner and outer sides of the surface  $S_b$ , respectively, due to the discontinuity of the density of 0-species on the surface  $S_b$ . Therefore, the virial theorem (1) with use of (6) provides

the following relation:

$$\begin{aligned} \oint_{\partial V} P_1^{w_a} \mathbf{r} \cdot d\mathbf{S} &= \oint_{\partial V} P_1 \mathbf{r} \cdot d\mathbf{S} \\ &= \oint_{\partial V_a} P_1 \mathbf{r} \cdot d\mathbf{S} + \oint_{\partial V_b} P_1 \mathbf{r} \cdot d\mathbf{S} + 3V_b [P_1(S_b^{\text{out}}) - P_1(S_b^{\text{in}})]. \end{aligned} \quad (9)$$

Here,  $P_1(S_b^{\text{in}}) = P_{1b}$  and  $P_1(S_b^{\text{out}}) = P_{1a}$  are the pressures just inside and outside of the surface  $S_b$  of the volume  $V_b$ , respectively. Since  $P_1^{w_a} = P_{1a}$ , the partial pressure  $P_1(\mathbf{r})$  in the a- and b-domains is related each other through the following equations:

$$P_1^{w_a} = P_{1a} = P_{1b} + \Gamma_1 \quad (11)$$

$$\Gamma_1 \equiv P_{1a} - P_{1b}, \quad (12)$$

which are obtained from (10) with use of (5). The partial pressure  $P_1(\mathbf{r})$  becomes uniform in  $V_a$  and  $V_b$ , but has a pressure difference  $\Gamma_1$  between them. Here, the partial pressure  $P_{1a}$  is determined by the virial equation

$$P_{1a} = k_B T \rho_{1a} - \frac{1}{6} \rho_{1a}^2 \int_{V_a} r \frac{dv_{11}(r)}{dr} g_{11}(r) d\mathbf{r}, \quad (13)$$

which is described by the radial distribution function  $g_1(r)$  and binary interatomic potential for the domain-a, and  $P_{0b}$  is given by (7b) for the domain-b as

$$\begin{aligned} P_{0b} &= k_B T \rho_{0b} - \frac{1}{6} \rho_{0b}^2 \int r \frac{dv_{00}(r)}{dr} g_{00}(r) d\mathbf{r} \\ &+ \sum_{i \in \alpha b} \langle \mathbf{r}_i \cdot \mathbf{F}_i^{\alpha b} \rangle / 3V_b, \end{aligned} \quad (14)$$

since there is a uniform mixture of 0- and 1-species in the domain-b.

On the other hand for the case of 0-species, due to the density discontinuity on the surface  $S_b (= \partial V_b)$  in the volume  $V$ , the surface of pressure discontinuity mentioned above appears to be coincident with  $S_b$ . Therefore, we shift this discontinuity surface to  $S_{b'}$  inside of  $S_b$  by  $\epsilon$ , and get a final relation by taking the limit  $\epsilon \rightarrow 0$  with use of  $P_0(S_{b'}^{\text{in}}) = P_{0b}$ ,  $\lim_{\epsilon \rightarrow 0} P_0(S_{b'}^{\text{out}}) = P_0(S_b^{\text{in}})$  and  $3V_{b'} = \oint_{S_{b'}} \mathbf{r} \cdot d\mathbf{S}$ :

$$\begin{aligned} \oint_{\partial V_b} P_0^{w_b} \mathbf{r} \cdot d\mathbf{S} &= 3 \lim_{\epsilon \rightarrow 0} \{ (S_b \epsilon) P_0^{w_b} + (V_b - S_b \epsilon) P_{0b} \\ &+ V_{b'} [P_0(S_{b'}^{\text{out}}) - P_0(S_{b'}^{\text{in}})] \} \\ &= 3V_b P_{0b} + 3V_b [P_0(S_b^{\text{in}}) - P_{0b}], \end{aligned} \quad (15)$$

which is derived from the virial theorem (1) with use of (6). Here, the pressure contribution of a volume  $S_b \epsilon$  disappears in the limit  $\epsilon \rightarrow 0$  and  $P_0(S_b^{\text{in}})$  is the pressure on the wall b exerted by the 0-species particles. Hence, we get the final result:

$$P_0^{w_b} = P_0(S_b^{\text{in}}) = P_{0b} + \Gamma_0 \quad (17)$$

$$\Gamma_0 \equiv P_0(S_b^{\text{in}}) - P_{0b}. \quad (18)$$

The pressure  $P_0(\mathbf{r})$  provides  $P_0^{w_b}$  to be equal with the osmotic pressure on the membrane  $S_b$ , and has a pressure

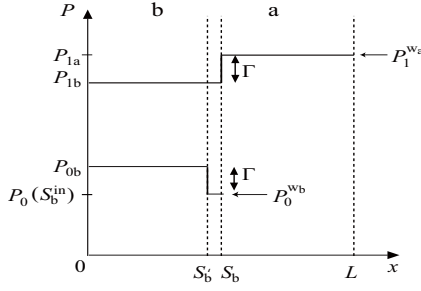


FIG. 2. The pressure relations for the osmotic system for a cubic volume  $L^3$  with a semipermeable membrane  $S_b$  at  $x = L/2$ . The b-domain involves particles of 0- and 1-species, while the a-domain contains 1-species particles only. The surface of pressure discontinuity of 0-species is shifted towards the origin by  $\epsilon$  as shown by  $S_{b'}$ .

difference  $\Gamma_0$  in comparison with the internal pressure  $P_{0b}$  in  $V_b$ .

Because the osmotic pressure  $P^{\text{osm}}$  is the pressure on the wall b exerted by the 0-species particles, it must satisfy the next relation (see Appendix A for this proof):

$$P_0^{\text{wb}} = P^{\text{osm}} \equiv (P_{0b} + P_{1b}) - P_{1a}, \quad (19)$$

which leads to the following condition:

$$\Gamma_0 + \Gamma_1 = 0. \quad (20)$$

Owing to the relation  $P_{1a} = P_1^{\text{wa}}$ , Eq. (19) is rewritten in the form:

$$P_0^{\text{wb}} + P_1^{\text{wa}} = P \equiv P_{0b} + P_{1b}. \quad (21)$$

The relations, (11), (17), (20) and (21), have been obtained by Itano *et al.* by means of the molecular dynamics method using the perfectly reflective wall [3].

In Fig.1, the osmotic system is represented as a general volume shape; the volume shape can be deformed to the cubic volume  $V = L^3$  put on the rectangular coordinates  $x = y = z = L$  with a plane semipermeable membrane at  $x = L/2$ . The region  $(0 < x < L/2)$  is the b-domain involving particles of 0- and 1-species, while the region  $(L/2 < x < L)$  becomes the a-domain containing 1-species particles only. Naturally, the relations for  $P_1^{\text{wa}}$  and  $P_0^{\text{wb}}$  given by (11) and (17), respectively, are established for this cubic volume along the  $x$ -axis, as can be shown in the similar manner above. The following pressure relations are shown in Fig.2 for this osmotic system:

$$P_1^{\text{wa}} = P_{1b} + \Gamma \quad (22a)$$

$$P_0^{\text{wb}} = P_{0b} - \Gamma \quad (22b)$$

with  $\Gamma \equiv \Gamma_1 = -\Gamma_0$ . The partial pressure  $P_1(x)$  leads to  $P_1^{\text{wa}} = P_{1a}$  in the domain-a, and becomes identical with the partial pressure  $P_{1b}$  in the domain-b with a pressure jump  $\Gamma$  at the surface  $\partial V_b$ . In a similar way, the wall pressure  $P_0^{\text{wb}}$  for 0-species particles has a difference  $\Gamma$  compared to the internal pressure  $P_{0b}$  in the domain-b.

We can understand why the pressure difference appears at the semipermeable membrane physically for the case of the experiment of Itano *et al.*, as follows. The density of solute molecules (0-species particles) is zero in  $V_a$  and jumps to  $\rho_{0b}$  in  $V_b$ , with the membrane forming a discontinuity surface in  $V$ . Therefore, the total sum of solvent-solute interactions (strong repulsive potential) caused by all solute particles in  $V_b$  behaves like a wall potential to the solvent particles in  $V_a$ , producing the pressure  $\Gamma$  on the solvent particles in  $V_a$ ; this is the reason that the solvent pressure is higher in  $V_a$  than in  $V_b$ . As the reaction to this acting pressure  $\Gamma$  on the solvent, the solvent particles in  $V_a$  support the solute pressure  $P_{0b}$  in  $V_b$  together with the confining pressure  $P_0^{\text{wb}}$  at the membrane. This is the reason that the osmotic pressure  $P_0^{\text{wb}}$  to support the solute particles in  $V_b$  is lower than the hydrostatic solute pressure  $P_{0b}$  by  $\Gamma$ . Itano *et al.* [3] have calculated the total interaction force  $\Delta U L^2$  exerted on the entire solvent by the entire solute with a surface  $L^2$ : their  $\Delta U (> 0)$  is identical with  $\Gamma$ . Also, the fact above mentioned is the reason that the surface of pressure discontinuity in the volume  $V$  should be taken into account at the semipermeable membrane for the 0-species particles as well as the 1-species particles in the derivation of (11) and (17) because of the action and reaction between these two species.

Now, equations, (22a) and (22b), are written as follows:

$$P^{\text{wa}} = k_B T \rho_{1b} - \frac{1}{6} \rho_{1b}^2 \int r \frac{dv_{11}(r)}{dr} g_{11}(r) d\mathbf{r} - \frac{1}{3} \rho_{0b} \rho_{1b} \int r \frac{dv_{01}(r)}{dr} g_{01}(r) d\mathbf{r} + \Delta, \quad (23)$$

$$P^{\text{wb}} = P_{0b} - \Gamma = k_B T \rho_{0b} - \frac{1}{6} \rho_{0b}^2 \int r \frac{dv_{00}(r)}{dr} g_{00}(r) d\mathbf{r} - \Delta, \quad (24)$$

with use of the definition of partial pressures  $P_{\alpha b}$  given by (14) with help of (8). Here,  $\Delta \equiv \Gamma - \sum_{i \in 0b} \langle \mathbf{r}_i \cdot \mathbf{F}_i^{0b} \rangle / 3V_b$ . In the dilute solution over a wide range of concentrations, computer simulation experiments [3, 9] have demonstrated the validity of van't Hoff's law:

$$P^{\text{osm}} = P_{0b} - \Gamma = k_B T \rho_{0b}. \quad (25)$$

which means  $\Delta = 0$  in (24). In another point of view, if we introduce the following assumption for a dilute solution:

$$\Gamma = \sum_{i \in 0b} \langle \mathbf{r}_i \cdot \mathbf{F}_i^{0b} \rangle / 3V_b, \quad (26)$$

Eq. (24) in the dilute solution is taken to provide van't Hoff's law (25).

Furthermore, we show below that the partial pressure  $P_\alpha$  even in liquids can be measurable. Note that the osmotic system is separated into two coupled systems consisting of a pure fluid and a fluid mixture when we cover the semipermeable membrane with a membrane impermeable to 1-species from the domain-a side in the osmotic

equilibrium state. Also, it should be noted that the external force condition (A1) to keep the osmotic system steady holds too in the two coupled systems as shown below. These new two systems are coupled with each other in a way that the 1-species internal pressure of one system works as an external pressure to the other to sustain equilibrium. Now, the 1-species particles do not move through the semipermeable membrane and the osmotic system is changed to the separated two systems, a fluid mixture with a pressure  $P_{0b} + P_{1b}$  confined in the volume  $V_b$  and a pure fluid with a pressure  $P_{1a}$  in the volume  $V_a$ . Therefore, the 0-species pressure on the semipermeable membrane increases by  $\Gamma$  compared to the osmotic system, since  $P_0^{wb} = P_{0b}$  for this mixture in  $V_b$ . On the other hand, the membrane impermeable to 1-species covering the semipermeable membrane from the pure fluid side divides the 1-species particles by confining them in  $V_a$  and  $V_b$ , and feels the pressure  $\Gamma$  in the negative x direction due to the pressure difference of 1-species as shown in Fig.2. Therefore, this membrane is pushed onto the semipermeable membrane by the pressure  $\Gamma$ , which is balanced to the increased pressure  $\Gamma$  of the semipermeable membrane in the positive x-direction. As a result, this fact provides the means to measure the pressure difference  $\Gamma$  involved in (22a) and (22b). Thus, the partial pressures  $P_{\alpha b}$  in  $V_b$  can be obtained by using values of the osmotic pressure  $P_0^{wb}$  and  $P_1^{wa}$ , which are observable, with the help of (22a) and (22b). In addition, the pressure difference  $\Gamma = \Delta U$  can be calculated by evaluating the pressure difference between both sides of the membrane impermeable to 1-species with aids of the MD simulation, instead of using the solute-solvent interaction force as was done by Itano *et. al.* [3].

In this way, it is shown that partial pressures,  $P_{\alpha b}$ , are measurable on the basis of the osmotic pressure. As a result, the law of partial pressures (7) is shown meaningful even in real gases and liquids as well as in ideal gases on the basis of the relations in the osmotic system, which relates the partial pressures to the wall pressures,  $P_0^{wa}$  and  $P_1^{wb}$ . In other words, owing to the pressure difference  $\Gamma$  on the membrane, the law of partial pressures for this osmotic system may be interpreted as expressed in the following forms:  $P_1^{wa} = P_{1b} + \Gamma$ ,  $P_0^{wb} = P_{0b} - \Gamma$  and  $P = P_1^{wa} + P_0^{wb} = P_{1b} + P_{0b}$ , and Eq. (7) is recovered when  $V_a = 0$ .

### III. OSMOTIC SYSTEMS CONSISTING OF MANY KINDS OF SPECIES

In §II, we treated an osmotic system consisting of two types of species, 0 and 1; here, we increase types of species such as 0, 1, 2, ...,  $M$ , and add 0-species particles also in the domain-a. In this case, we obtain the following relations for all species except 0 ( $i = 1, \dots, M$ ):

$$P_i^{wa} = P_{ia} = P_{ib} + \Gamma_i. \quad (27)$$

Here,  $\Gamma_i \equiv P_i(S_b^{\text{out}}) - P_i(S_b^{\text{in}}) = P_{ia} - P_{ib}$ . On the other hand, the following equation is established for the wall pressure  $P_0^{wb}$  confining the 0-species particles:

$$P_0^{wb} = P_{0b} - P_{0a} + \Gamma_0 = P_0(S_b^{\text{in}}) - P_{0a}. \quad (28)$$

Eq. (28) involves  $P_{0a}$  in comparison with (17) due to the presence of the 0-species particles in the domain-a of this system. Since the difference between the pressure  $P_b$  and the pressure  $P_a = P_b - P_{0b} + \sum_{i=1}^M \Gamma_i + P_{0a}$  brings about the osmotic pressure  $P^{\text{osm}} = P_0^{wb} = P_b - P_a$ , we obtain the condition  $\sum_{i=0}^M \Gamma_i = 0$  for  $\Gamma_i$ . On the other hand, Eq. (21) is written in the another form:  $P_0^{wb} + \sum_{i=0}^M P_i^{wa} = P_b$ .

In physiology, the partial pressure of water in solutions is important to see balance of water in body fluids. Water balance between ‘a’ and ‘b’ solutions separated by a membrane is maintained under the condition for the partial pressures of water:

$$P_{\text{water-a}} = P_{\text{water-b}} + \Gamma \quad (29)$$

with a proper pressure difference  $\Gamma$ ; unless this condition is satisfied, the osmotic flow of water occurs. For example, when  $M$  kinds of impermeable solutes are dissolved in both a- and b-domains with partial pressures,  $P_{ia}$  and  $P_{ib}$ , keeping the relation  $P_i^{wb} = P_{ib} - P_{ia} - \Gamma_i$ , the above pressure difference is expressed by  $\Gamma = \sum_{i=1}^M \Gamma_i$  as shown in Appendix C.

In this situation, we consider a special state of the above osmotic system, where the particles in the domain-a constitute the gas phase, and the particles in the domain-b become the liquid phase [10, 11] assuming that all types of species are volatile. If this osmotic system maintains this two-phase equilibrium even when the confining pressure  $P_0^{wb}$  of 0-species becomes zero, we can take this state to be in the vapor-liquid equilibrium; that is, the condition,  $P_0^{wb} = 0$ , leads to the condition for the two-phase equilibrium  $P_b = P_a$ . From the condition:  $P_0^{wb} = P_0(S_b^{\text{in}}) - P_{0a} = 0$ , there results the following relation  $P_0^{wa} = P_{0a} = P_0(S_b^{\text{in}})$ . Hence, for all species including 0-species ( $i = 0, \dots, M$ ), we obtain the relation between partial pressures of the liquid- and gas-phases:

$$P_i^{wa} = P_{ib} + \Gamma_i = P_{ia}, \quad (30)$$

with the condition  $\sum_{i=0}^M \Gamma_i = 0$ . Moreover, the non-volatility of  $\alpha$ -species can be defined by the relation:  $P_\alpha^{wa} = P_\alpha^{wb} = P_\alpha(S_b^{\text{in}}) = P_{\alpha b} + \Gamma_\alpha = 0$  from (28).

In the vapor-liquid equilibrium, there are two approximate theories in a dilute solution; Henry’s law and Raoult’s law, which are valid only in the dilute limit. In contrast with these laws based on the chemical potential, Eq.(30) is valid without any condition since it is based on the rigorous virial theorem. Here, let us consider the solubility of a gas (1-species) in a liquid (0-species). In this problem, the vapor pressure of a liquid can be neglected compared to the gas pressure  $P_{1a}$  in the gas phase

[10, 11], that is, the 0-species liquid is approximated to be non-volatile as is written in the form:

$$P_{0b} = k_B T \rho_{0b} - \frac{1}{6} \rho_{0b}^2 \int r \frac{dv_{00}(r)}{dr} g_{00}(r) d\mathbf{r} + \sum_{i \in 0b} \langle \mathbf{r}_i \cdot \mathbf{F}_i^{0b} \rangle / 3V_b = \Gamma, \quad (31)$$

since the non-volatility is defined by the relation:  $P_0^{wa} = P_{0b} - \Gamma = 0$ . Therefore, the gas-liquid equilibrium is described by the following equation:

$$P_{1a} = P_{1b} + \Gamma = k_B T \rho_b - \frac{1}{6} \sum_{\alpha, \beta} \rho_{\alpha b} \rho_{\beta b} \int r \frac{dv_{\alpha\beta}(r)}{dr} g_{\alpha\beta}(r) d\mathbf{r}, \quad (32)$$

which is obtained by the use of (14), (31) and (8). Here, Eq. (31) for a dilute solution is reduced to

$$k_B T \rho_{0b} - \frac{1}{6} \rho_{0b}^2 \int r \frac{dv_{00}(r)}{dr} g_{00}(r) d\mathbf{r} = 0, \quad (33)$$

when we use the assumption (26). Therefore, for a dilute solution Eq. (33) makes (32) in the simple form:

$$P_{1a} = x_{1b} \cdot \left[ k_B T \rho_b - \frac{1}{3} \rho_b^2 \int r \frac{dv_{01}(r)}{dr} g_{01}(r) d\mathbf{r} \right], \quad (34)$$

which is nothing but Henry's law. Note that the Eq. (32) can be applied to determine the solubility  $x_{1b}$  of a gas at any pressure  $P_{1a}$  under the non-volatile approximation (31) in contrast with Henry's law (34) which is only valid in the dilute solution. Next, let us consider the vapor-liquid equilibrium in a solution consisting of 0-liquid and 1-solutes, where the vapor-liquid equilibrium is described by a set of equations:

$$P_1^{wa} = P_{1a} = P_{1b} + \Gamma \quad (35a)$$

$$P_0^{wa} = P_{0a} = P_{0b} - \Gamma. \quad (35b)$$

With help of (24), it is shown for a dilute solution that the assumption (26) produces Raoult's law from (35b) as follows:

$$P_{0a} = x_{0b} P_{0a}^0, \quad (36)$$

with the vapor pressure of a pure liquid,  $P_{0a}^0 \equiv k_B T \rho_b - \frac{1}{6} \rho_b^2 \int r dv_{00}(r)/dr g_{00}(r) d\mathbf{r}$ , while Eq. (35a) leads to Henry's law (34). It should be emphasized that the assumption (26) is valid for two different problems; one is the solubility problem where  $x_{0b} = 0$  and the other is the vapor-liquid equilibrium where  $x_{0b} \approx 1$ .

#### IV. DISCUSSION AND CONCLUSION

In §II, we have shown that the law of partial pressures can be applied to liquid mixture using the virial equation for particles with binary interactions. However, this brings no essential restriction on its applicability for

systems. Even for mixtures with more complicated interactions (molecules for example), the partial pressure is defined by the wall pressure  $P_\alpha^w$  exerted by its constituent species as (2), and the virial pressure  $P_\alpha$  is determined by (5b) for general potentials including even ternary interactions for example.

In §II, the wall potentials are assumed to be perfectly elastic and become abruptly infinite at surfaces, but in reality they are short-range repulsive potentials which interact with inner particles to some range in the volume. The influence of the wall potential with a finite range  $\Delta x$  can be estimated by  $P^w = P(1 - \frac{S\Delta x}{V})$  with the surface area  $S$  of the volume  $V$  (see Appendix B): we can see that the wall-potential effect disappears in accord with increase of the volume  $V$  compared to  $S\Delta x$ , even when the particle density shows a gradual increase up to the uniform density in the distance of the order  $\Delta x$  from the wall. In a similar way, a finite range of the membrane potential produces a continuous change in  $P_0(\mathbf{r})$ , which is zero at the membrane surface  $S_b$  and becomes  $P_0(S_{b-\Delta x}) = P_{0b}$  in the inner region  $\Delta x$  from  $S_b$ . Here,  $S_{b-\Delta x}$  denotes the surface  $S_b$  shifted inside by  $\Delta x$ . However the pressure difference  $\Gamma_0$  near the membrane is unchanged, since the osmotic pressure is independent of the form of the purely repulsive potential chosen for the membrane potential [12]. This is also due to the fact that the microscopic structure of pressure profile does not contribute thermodynamically to the pressure difference  $\Gamma_0$  as shown in (B3). In detail, the meaning of (17) for this continuous case is expressed as

$$P^{osm} = P_0^{wb} \neq P_0(S_{b-\Delta x}) = P_0^{wb} + \Gamma = P_{0b}. \quad (37)$$

That is to say, the partial pressure  $P_0(\mathbf{r})$  supports the osmotic pressure  $P_0^{wb}$  and the acting pressure  $\Gamma (\equiv -\Gamma_0)$  of the 0-species particles on the 1-species particles in  $V_a$  as mentioned in §I, and becomes a constant pressure  $P_0^{wb} + \Gamma$ , which is equal to  $P_{0b}$ , at a near distance  $\Delta x$  from the membrane. Thus, the wall pressure  $P_0^{wb}$  is different from the inner pressure  $P_{0b}$  by  $\Gamma$ , too, in the continuous case.

Until now, the law of partial pressures is supposed to be applicable only to ideal gases, and the definition of the partial pressures in liquids is insignificant because of some arbitrariness in the division of the total pressure into several parts. In this investigation, we have shown that the partial pressure can be defined uniquely as each wall pressure exerted by a component in the system, and is an important observable physical quantity. As a consequence of this definition, the law of the partial pressures is applicable to liquid mixtures with strong interactions as well as to ideal gases. Furthermore, it has been shown here that the partial pressures play an important role to see structures of the gas-liquid phase equilibrium in addition to the osmotic system: the total pressure balance between the gas- and liquid-phases is established by each partial-pressure balance for a component in the gas- and liquid-phases, respectively, as is described in the relation:  $P_{ia} = P_{ib} + \Gamma_i$ . The non-volatility of  $\alpha$ -species in a solution is defined by  $P_\alpha + \Gamma_\alpha = 0$  on the basis of the definition of

partial pressures.

### Appendix A: Proof of (19)

In an osmotic system with the cubic volume as shown in Fig.2, three *external* forces,  $F(0)$ ,  $F(L/2)$  and  $F(L)$ , must be applied to the three surfaces,  $S(0)$ ,  $S(L/2)$  and  $S(L)$ , located at  $x = 0$ ,  $x = L/2$  and  $x = L$ , respectively, to keep this osmotic system steady;

$$F(0)\mathbf{e}_x = [F(L/2) + F(L)]\mathbf{e}_x, \quad (\text{A1})$$

with  $\mathbf{e}_x$  being the unit vector of the x-axis. Since  $F(0)/L^2 = P_0^w(0) + P_1^w(0) = P_{0b} + P_{1b}$  and  $F(L)/L^2 = P_1^w(L) = P_{1a}$ , we obtain  $F(L/2)/L^2 = P_{0b} + P_{1b} - P_{1a} = P^{\text{osm}}$ . Note that this relation is valid even when the solvent molecules (1-species) interact with the semipermeable membrane  $S(L/2)$ , since  $F(L/2)/L^2$  is determined by the interactions of molecules only with the walls,  $S(0)$  and  $S(L)$ , irrespective of the membrane wall  $S(L/2)$ . Therefore, Eq.(19) is valid without any condition, since  $F(L/2)/L^2 = P_0^w(L/2) \equiv P_0^{wb}$ . In fact, in the standard treatment in MD simulation the osmotic pressure is determined by the wall pressure  $P_0^{wb}$  rather than by the pressure difference for purposes of accuracy, [3, 12] even when the solvent molecules interact with the semipermeable membrane [9, 10, 13].

### Appendix B: Influence of wall potential with a finite range

Thermodynamically, the wall potential  $U^w$  confining a fluid to a finite volume  $V$  is assumed to be perfectly elastic and becomes abruptly infinite at the surface  $\partial V$ . In reality the wall has short-range repulsive potentials which interact with inner particles to some range in the volume. Therefore, we obtain  $P^w = P = 0$  if Eq. (3) is simply applied because of  $P = 0$  at the surface  $\partial V$ . The influence of the wall potential with a finite range has been examined by Green [14], where he showed that at the surface  $S'$  located in the distance  $\Delta x$  inner from the wall,  $P^w = P$  is established and  $P^w = \int_0^{\Delta x} \frac{dP(x)}{dx} dx$  for the one dimension case. Since the influence of the wall disappears at the surface  $S' (= \partial V')$  located in the distance  $\Delta x$  from the wall with an area  $S (= \partial V)$ , this influence is described as follows. Because the hydrostatic pressure  $P(\mathbf{r})$  is zero at the surface of the wall, there results,  $0 = \oint_S \mathbf{Pr} \cdot d\mathbf{S} = [\oint_S - \oint_{S'}] \mathbf{Pr} \cdot d\mathbf{S} + \oint_{S'} \mathbf{Pr} \cdot d\mathbf{S} = \int_{S\Delta x} \nabla \cdot (\mathbf{r}P) d\mathbf{r} + \int_{V'} \nabla \cdot (\mathbf{r}P) d\mathbf{r}$ . Here,  $-\int_{S\Delta x} \nabla \cdot (\mathbf{r}P) d\mathbf{r}$  denotes the pressure effect exerted by the wall on the particles via a distortion in  $P(\mathbf{r})$  caused by the wall potential  $U^w$ . Therefore, we

obtain

$$\begin{aligned} \oint_S P^w \mathbf{r} \cdot d\mathbf{S} &= - \int_{S\Delta x} \nabla \cdot (\mathbf{r}P) d\mathbf{r} \\ &= \int_{V'} \nabla \cdot (\mathbf{r}P) d\mathbf{r} = 3P(V - S\Delta x), \end{aligned} \quad (\text{B1})$$

owing to  $P(S') = P$ . That is,

$$P^w = P \left( 1 - \frac{S\Delta x}{V} \right). \quad (\text{B2})$$

The influence of the wall may disappear when the volume  $V$  becomes infinite, and the pressure on the wall exerted by particles is taken as that given by the virial equation; this is the meaning of the virial equation (4) for a real wall potential.

When the pressure  $P$  has a step-function like discontinuity on the surface  $S (= \partial V_b)$  of the volume  $V_b$  involved in the volume  $V$ , a formula to calculate the surface integral is given by (6). Here, we consider the case where the pressure  $P$  increases continuously in the narrow domain between the two surfaces,  $S_{+\Delta x}$  and  $S_{-\Delta x}$  with  $\Delta x$  being the order of the interatomic potential range, instead of a step-function like discontinuity on the surface  $S$ . Here,  $S_{+\Delta x}$  and  $S_{-\Delta x}$  denote a surface  $S$  shifted outside by  $\Delta x$  and that shifted inside, respectively. In a similar way to obtain (B2), we can evaluate the surface integral  $\oint_{\partial V} \mathbf{Pr} \cdot d\mathbf{S}$  for this case on the basis of an identity:  $\oint_{\partial V} \mathbf{Pr} \cdot d\mathbf{S} = [\oint_{\partial V} \mathbf{Pr} \cdot d\mathbf{S} - \oint_{S_{+\Delta x}} \mathbf{Pr} \cdot d\mathbf{S}] + [\oint_{S_{+\Delta x}} \mathbf{Pr} \cdot d\mathbf{S} - \oint_{S_{-\Delta x}} \mathbf{Pr} \cdot d\mathbf{S}] + \oint_{S_{-\Delta x}} \mathbf{Pr} \cdot d\mathbf{S}$ . If we neglect quantities of the order  $S\Delta x/V$ , we obtain from the above identity

$$\begin{aligned} \oint_{\partial V} \mathbf{Pr} \cdot d\mathbf{S} &= \oint_{\partial V_a} \mathbf{Pr} \cdot d\mathbf{S} + \oint_{\partial V_b} \mathbf{Pr} \cdot d\mathbf{S} \\ &\quad + [P(S_{+\Delta x}) - P(S_{-\Delta x})] \oint_{\partial V_b} \mathbf{r} \cdot d\mathbf{S}. \end{aligned} \quad (\text{B3})$$

### Appendix C: Water balance in solutions with several solutes

A membrane separates solutions into 'a' and 'b' domains involving water (species-0) as a solvent. In solutions,  $M$  kinds of *impermeable* solutes are dissolved in both a- and b-domains with partial pressures,  $P_{ia}$  and  $P_{ib}$ , keeping the relation  $P_i^{wb} = P_{ib} - P_{ia} - \Gamma_i$ . In addition,  $M'$  kinds of *permeable* solutes are dissolved in these domains with partial pressures,  $\tilde{P}_{ja}$  and  $\tilde{P}_{jb}$ , keeping the relation  $P_j^{wa} = \tilde{P}_{ja} = \tilde{P}_{jb} + \tilde{\Gamma}_j$ . Then, the osmotic pressure of this system is given by  $P^{\text{osm}} = P^{wb} \equiv \sum_{i=1}^M P_i^{wb} = P_b - P_a$ . Here, the total pressure of the domain- $\alpha$  ( $\alpha = a$  or  $b$ ) is defined by  $P_\alpha \equiv P_\alpha^s + P_{0\alpha}$  with the solute pressure  $P_\alpha^s \equiv \sum_{i=1}^M P_{i\alpha} + \sum_{j=1}^{M'} \tilde{P}_{j\alpha}$ . Water balance is established under the condition  $P_0^{wa} = P_{0a} = P_{0b} + \Gamma$  with  $\Gamma = \sum_{i=1}^M \Gamma_i - \sum_{j=1}^{M'} \tilde{\Gamma}_j$ . The osmotic pressure is rewritten also as  $P^{wb} = P_b^s - P_a^s - \Gamma$ .

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